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論文内容の要旨

In the present thesis, the results of the photoemission spectroscopy for some rare earth compounds and thin film systems of 3*d* transition metal have been described. Photoemission spectroscopy is very useful and direct method for studying both the electronic and magnetic structures of the systems. Synchrotron radiation plays an important role in the photoemission study where the higher photon flux, light polarization and selection of particular photon energy are advantageous.

In order to perform the present experiments, the VGESCALAB220i-XL spectromicroscopy system was mainly used. During the present study, the improvement of the system has been performed as follows. First, a chamber for sample preparation and epitaxial growth of thin film was developed. The LEED optics, water-cooled evaporators, thickness monitor and magnetic coil were installed in that preparation chamber. The manipulator was also improved by constructing a He-cryostat for performing temperature dependent photoemission experiments. Several experiments were thus successfully carried out after finishing all those improvements. The performance of the cryostat was checked by measuring the core level photoemission in Eu-compound. The result will be shown in appendix part of the thesis.

Core level photoemission studies of TmX compounds:

One of the main parts of this thesis is to describe the study of the core level photoemission for rare earth TmX (X=S, Se and Te) compounds. Rare earth compounds are known to show their remarkably different physical, magnetic and electronic properties. Among these mixed-valent systems, TmS is known to be mostly trivalent, TmTe is mostly divalent and TmSe is intermediate valent. In the rare earth system, the well localized 4*f* electrons are strongly interacted with the core hole in the final state of photoemission. The effect of this interaction shows multiplet splitting, lifetime broadening effect, exchange splitting and configuration interaction in the final state of photoemission. Interpretation of the core level photoemission through those final state effects gives the information of interaction between core hole and 4*f* electrons. This interaction also depends on the nature of the wave function of core level and the valence shell. For TmX system, no systematic experiment of different core levels (Tm4*d*, 4*p*, 5*p*, 3*d*) has been performed so far. In the present study, photoemission experiments including resonant effects were performed for these core levels in all TmX compounds. A rich information about the final state effects (mentioned above) and valence fluctuation in core level photoemission was obtained. Comparison with the calculation is also given to get better understanding of the experimental results. The results are summarized below.

1. Tm4*d* shows multiplet structures and each multiplet shows different resonance

enhancement depending on the excitation conditions around the Tm 3*d*-4*f* absorption edges ($h\nu$=1450-1550eV). The lifetime broadening effect depending on the binding energy is present in both the on- and off-resonant photoemission. Through this experiment, the divalent and trivalent components in Tm4*d* were successfully separated and identified.

2. In case of 5*p* level, the values of spin-orbit splitting of two valences were estimated by the help of resonant effect and calculation. The values obtained from the present experiment are considered more reasonable than those of the previous reports.
3. In case of 4*p* XPS, the complex spectral features are explained by the configuration interaction phenomenon.
4. Tm3*d* level was also measured for studying the effect of 3*d*-4*f* interaction. It was found that the spin-orbit peaks are locally broadened due to the existence of multiplet structures.

Photoemission study of magnetic thin films:

It is now well known that the ultrathin films in nanometer range of 3*d*-materials often show very interesting and striking magnetic properties different from the bulk. Magnetic dichroism in photoemission, where two spectra are taken for two different magnetized states or light polarization states, is considered to be one of the most powerful methods to study thin film magnetism.

1. Ni/Co system: The reasons why the Ni/Co system was studied are as the followings. At first, in order to get the information of pure Ni3d states without any interaction with the substrate, Co substrate was suitable rather than Cu. In the previous result of thinner Ni film on Cu(001), the Ni 6eV satellite structures are overlapped with the tail of the broad Cu3d emission. Secondly, it is interesting to know whether the resonant effect (around the Ni 3p-3d excitation region) on the magnetic dichroism signal for the valence band of Ni-thin film system occurs or not. Finally, it is very curious to study the capability of epitaxial growth and corresponding magnetic phases of Ni on ferromagnetic Co.

The dichroism measurements of the Ni valence band photoemission conclude that the resonance effect is present on magnetic linear dichroism (MLD) for "6eV satellite". The present result is comparable with the previous MCDAD (Magnetic circular dichroism in angular distribution) results for bulk Ni (110) sample, but not MLDAD (L, linear) result. The MLD result of core level further shows that the Ni and Co are ferromagnetically coupled. The present result indicates that it is possible to magnetize the Ni film of 2.3, 8 and 11ML with in the surface plane (in-plane magnetization).

2. Oxidized Co film: The effect of oxidization for magnetic surface is very important

in magnetism study. In order to study the modification of electronic and magnetic structures of oxidized Co film, the Co2p core level photoemission spectra were measured. It was found that the behavior of the early oxidization followed by saturated CoO formation was different depending on the Co-thickness. Thinner films are more reactive and show an earlier formation of CoO than that of thicker films. The present result is different from the previous one where thickness independent oxidization in the early stage was reported. In the present study, two types of CoO phase depending on the thickness were found. The CoO phases are two-dimensional (2D) and three-dimensional (3D). It is predicted that the generally accepted CoO_6 model for 3D CoO phase might not be suitable for describing the core level spectra in case of 2D CoO phase.

Magnetic state of the oxidized Co film was studied by the MUDAD (U, unpolarized) measurement for Co2p level. MUDAD signal of Co2p level was found from the oxidized film even with higher exposure (40L). The result is different from the previous one. The present result concludes that the MD signal for O(40L)/Co(5ML) system probably is coming from the deeper and unaffected Co-site.

論文の審査結果の要旨

申請者の Nath 君から提出された博士論文は審査制度の確立した英文の学術雑誌に掲載された７編の原著論文の内容を含めて構成されている。論文は理論的背景、実験方法を含め６章から成っており、内容が非常に豊富で、丁寧に書かれている。

希土類化合物の光電子分光研究として、ツリウム(Tm)カルコゲン化合物（硫化物、セレン化物、テルル化物）を対象とし、Tm の 4f, 5p, 4d, 4p, 3d レベルを解析した。Nath 君は分子研 UVSOR 施設で分光器を選択して、励起光波長を Tm の 3d, 4d 内殻励起に合わせることで光電子放出における共鳴効果に注目した。共鳴させることで Tm の多電子構造の詳細、特に局在 4f 電子が係わる電子相関がより鮮明になる。このような系統的な研究は他の系においても少なく、Tm カルコゲン化合物においては 3d レベルを励起できる光源が少ないこともあって、断片的な研究があるのみであった。Nath 君は、表面部分とバルクにおける Tm の価数の違いなどについても詳しく調べ、これまで２価だけであるとされてきた表面成分に、実は３価も存在することを示した。また、Tm は硫化物でほぼ３価、テルル化物でほぼ２価、セレン化物では両者の中間の原子価をすべてのスペクトルで矛盾なく示すことがわかった。さらに、例えば、4d レベルを 3d-4f 共鳴で調べれば価数の分離が明確に行えること、5p レベルではスピン軌道相互作用の寄与を見積もることの重要性、4p レベルでは異なる電子配置の寄与を考慮すべき事　3d レベルではスピン軌道相互作用に加えて多重項の寄与を考慮すべき事など、内殻の違いによる特徴についても議論した。

磁性薄膜の光電子分光研究においては薄膜作成、試料冷却、磁場印加の装置開発・改良も自ら行っている。研究対象は Ni/Co/Cu 系と O/Co/Cu 系である。前者の系では放射光の直線偏光性を積極的に利用し、強磁性コバルト薄膜上の Ni エピタキシャル膜を電子構造と磁性の観点から研究し、Ni の価電子帯の光電子スペクトルに現れる "6eV" サテライトの磁気線二色性(MLD)を見つけ、さらにその共鳴現象をも発見した。解析から、Ni と Co は面内方向に強磁性的に相互作用していることを明らかにした。また、後者の系では放射光は用いない研究ではあるが、通常の X 線源でも磁性研究が可能であることを示した。磁性表面に対する初期酸化の影響を調べ、厚さに依存して二つの異なる相、すなわち２次元的なものと３次元的なものを見つけている。

提出論文の内容を慎重に審査した結果、Nath 君は電子相関の立場から希土類化合物と磁性薄膜の電子構造を、光電子分光によって明らかにできることを明確に議論し、この分野の他の研究者に対しても、新しい知見を与えていると判断され、博士（理学）の学位論文として充分に値するものであると、審査委員全員が結論した。

さらに、約３時間半、英語による口述試験を実施した。論文の説明及び質疑応答の中で、博士論文に関する専門分野ならびに基礎的な知識に関する質問を行った。Nath 君は、希土類化合物や磁性薄膜の研究の背景をよく理解していると同時に、光電子分光の関連分野についての基礎知識も確かなものであり、博士の学位を取るのに十分な学力を有していると判断した。学位論文の英文から判断して、英語表現に関する能力も学位を取るのに十分であると判断された。

また、公開発表会による最終審査にも合格した。